Dynamical Relativistic Effects in Photoionization: Spin-Orbit-Resolved Angular Distributions of Xenon 4*d* Photoelectrons near the Cooper Minimum

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INTRODUCTION

Relativistic effects in atoms have long been known to be important for photoionization dynamics at high **Z** [1,2]. At low and intermediate **Z**, where the predominant effect of relativity has been thought to be spin-orbit splitting of states into $j=l\pm1/2$ with differing threshold energies [1], recent advances in experiment [3] and theory [4] have demonstrated observable consequences of relativistic effects on photoionization dynamics. One of the most sensitive dynamical quantities in photoionization is the energy of a Cooper minimum, where the dipole matrix element for a particular channel goes through (or nearly goes through) zero. Relativistic interactions were predicted to significantly affect Cooper minima two decades ago [2]. Here, we report on a combined experimental and theoretical study of 4*d* photoionization in Xe where the spin-orbit components $4d_{5/2}$ and $4d_{3/2}$ are individually resolved. Experimentally this is difficult in the energy region of the $4d\rightarrow\varepsilon f$ Cooper minima because the dominant $d\rightarrow f$ contribution to the cross section is very small. In the absence of dynamical effects due to relativistic interactions, Cooper minima for $4d_{5/2}$ and $4d_{3/2}$ photoionization will be located at the same *kinetic energy*. Consequently, $\beta_{5/2}$ and $\beta_{3/2}$ would be identical as a function of photoelectron energy. However, the present measurements clearly exhibit differences in the β parameters and confirm the long-untested theoretical prediction of Kim *et al.* [2]. Furthermore, $\beta_{5/2}$ and $\beta_{3/2}$ differ not only in the immediate vicinity of the Cooper minima, but over a broad energy region, demonstrating the importance of relativistic effects in the photoionization of intermediate-**Z** atoms over a much larger energy range than previously suspected. The $4d\rightarrow\varepsilon f$ non-relativistic Cooper minimum splits into three minima relativistically; $4d_{5/2}\rightarrow\varepsilon f_{5/2}$, $4d_{5/2}\rightarrow\varepsilon f_{7/2}$ *and* $4d_{3/2}\rightarrow\varepsilon f_{5/2}$. Each would appear at the same photoelectron energy in the absence of dynamical effects resulting from relativistic interactions.

EXPERIMENTS

To check possible systematic errors related to a particular experimental method, the measurements were done independently with hemispherical and time-of-flight (TOF) electron spectrometers at two different undulator beamlines at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. One experiment was carried out at beamline 10.0.1 using an endstation designed for gas-phase angle-resolved studies based on the Scienta SES-200 hemispherical electron analyzer (HEA) [5]. The analyzer is rotatable in the perpendicular plane, allowing electron angular-distribution studies. Measurements at the θ angles of 0°, 54.7° and 90° were performed, and angular-distribution parameters were determined. In the TOF measurements, performed at ALS beamline 8.0, two analyzers are mounted in the perpendicular plane at θ=0° and θ=54.7°, allowing simultaneous measurements for accurate determination of β parameters [6]. To determine β parameters, the data were calibrated with the Ne-2*s* photoline, which has a fixed β value of 2. In both experiments, for most of the data, the photon energy was increased in 2-eV steps, because the energy splitting of the spin-orbit components is 2.0 eV. This approach permitted the measurement of $\beta_{5/2}$ and $\beta_{3/2}$ at the same photoelectron *kinetic energy*, and the difference $\beta_{3/2}$-$\beta_{5/2}$ could be calculated easily. At higher energies, where larger energy steps were used (TOF measurements only), continuous curves were interpolated through the measured values of β and used to estimate the difference $\beta_{3/2}$-$\beta_{5/2}$.

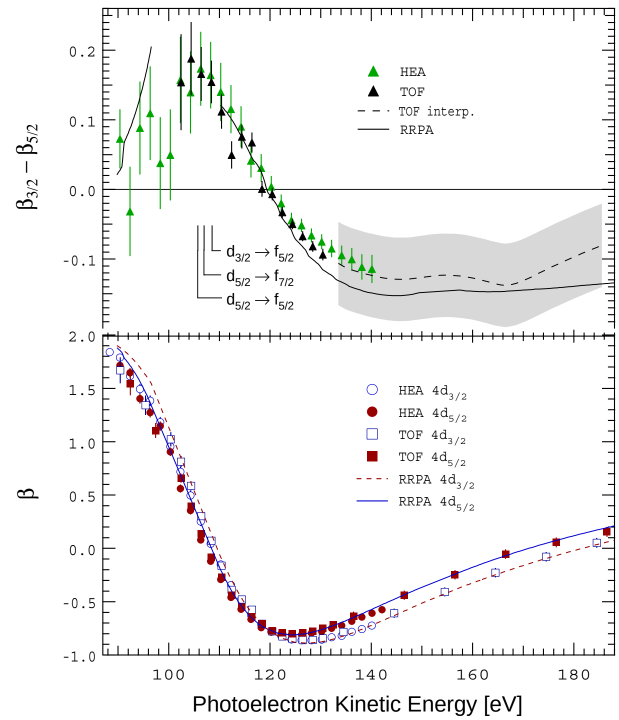

Figure 1. Lower panel: Photoelectron angular-distribution parameters, $\beta_{5/2}$ and $\beta_{3/2}$, for Xe 4*d* ionization as a function of photoelectron energy. The points are the present experiment and the curves are our theoretical results. Upper panel: $\beta_{3/2}$-$\beta_{5/2}$ as a function of photoelectron energy derived from the data in the lower panel. The dashed curve was obtained via interpolation of the TOF data, and the shaded area represents error bars. Omitted from theory is the region of the $4p \rightarrow ns,nd$ resonances. Also shown are theoretical predictions for the locations of the Cooper minima.

RESULTS

Calculations were performed using the relativistic random-phase approximation (RRPA) [7] based upon the Dirac Equation; relativistic effects are included on an *ab initio* basis. All relativistic single-excitation channels from the 4*s*, 4*p*, 4*d*, 5*s* and 5*p* subshells were included in the calculation, a total of 20 interacting channels. As noted above, in the absence of relativistic effects, β_j *must* be independent of *j* as a function of photoelectron energy. The present results for $\beta_{5/2}$ and $\beta_{3/2}$ as a function of photoelectron energy are shown in the lower panel of Fig. 1, where a clear difference is evident. To focus on this difference more clearly, values of $\beta_{3/2}$-$\beta_{5/2}$ are shown in the upper panel of Fig. 1, where zero corresponds to the nonrelativistic expectation. Also shown in Fig. 1 are the results of our RRPA calculations. The agreement is remarkably good between theory and experiment. The part missing from the theoretical curve is the $4p \rightarrow ns,nd$ resonance region where the theoretical results are affected by autoionization. There is also excellent agreement between the two sets of experimental results, providing confidence in the reliability of the measurements. Note particularly that the β-parameter curves are not simply shifted, but have different shapes, *e.g.*, $\beta_{3/2}$ goes lower than $\beta_{5/2}$, and the differences persist to higher energy. At still higher energies, recent work has shown that interchannel interactions are pervasive and often dominant for most subshells of most atoms at most energies [8], so much so that even the asymptotic form of the high-energy nonrelativistic photoionization cross section for non-*s*-states is altered. Thus, as long as 4*d* photoionization does not dominate the total cross section, significant interchannel interactions will modify the 4*d* transition amplitudes. But there is no reason to expect these interchannel interactions will modify each relativistic amplitude in the same way, *i.e.*, interchannel coupling will cause observable differences between $\beta_{3/2}$ and $\beta_{5/2}$ for *all* higher energies. Near threshold, it is also known $\beta_{3/2}$ and $\beta_{5/2}$ differ due to differing exchange interactions among the relativistic channels. Only in the shape-resonance region, 30-80-eV kinetic energy, are there no differences between $\beta_{3/2}$ and $\beta_{5/2}$, because the 4*d* cross section dominates here and the energy is high enough so exchange interactions are no longer important; interchannel interactions are negligible *only* in this narrow region. Thus, except for a small energy region near the 4*d* shape resonance, equality of $\beta_{3/2}$ and $\beta_{5/2}$ is the exception, not the rule.

CONCLUSIONS

Finally, there is no reason to suspect Xe 4*d* is a special case; the results found in this work should be quite general. We thus expect effects of relativistic interactions on interchannel coupling will be widespread over all intermediate-**Z** atoms. These effects also should be manifest in clusters, molecules, surfaces, and solids.

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